

REMARKS

By the present Amendment, Table 4 has been amended to correct the indication that Polyol D is within the definition of Polyol (C) consistent with the characterization shown in Tables 1-3. The claims, however, have not been amended as applicants respectively maintain that the claims are patentable over the cited prior art of record.

Based on the reasons set forth in the Official Action, applicants believe that the Examiner may not fully appreciate the significance of each of the recited features of the claims and therefore provide the following discussion. As recited in claim 1, one aspect of the present invention relates to a flexible polyurethane foam obtained by contacting a polyol composition (A) comprising 0.5 to 3 parts by weight of a polyetherpolyol (polyol (D)) having a defined amine value and a defined hydroxyl value that is produced by the addition of an alkylene oxide to at least one amine compound represented by defined formula (II) with an organic polyisocyanate. The polyol composition additionally comprises 0 to 99.5 parts by weight of defined polyol (B) and 0 to 99.5 parts by weight of defined polyol (C) with the polyols being in such a ratio that the sum is 100 parts by weight. Claim 4 recites the polyol composition, *per se*, using the same definitions and amounts.

The first point to recognize is that the defined polyol composition is designed to obtain a flexible polyurethane foam as explicitly recited in claim 1. A flexible polyurethane foam has a significance in the art and is understood to be different from rigid foams. It is for this reason that the flexible polyurethane foam of claim 1 is especially suitable as an automobile seat pad or sound insulating material as recited in certain claims of record. The understanding in the art that flexible polyurethane

foams are distinct from rigid foams is substantiated by reference to the attached Tables of Contents of "Polyurethane Handbook" (see sections 5 and 6) and "Handbook of Polymeric Foams and Foam Technology" (see sections 4 and 5).¹

The next point to consider is that the claims expressly recite that the polyol (D) be present in an amount of 0.5 to 3 parts by weight and is a polyetherpolyol having a defined amine value and a defined hydroxyl value that is produced by the addition of an alkylene oxide to at least one amine compound represented by defined formula (II). Defined polyol (B) and/or polyol (C) must also be present so that the total amount of polyol is 100 parts by weight.

When following the teachings of the present invention, a flexible polyurethane foam can be obtained that can exhibit reduced volatile amine emission and which has excellent characteristics as shown in the Examples in the Tables starting on page 33. For instance, Examples 2 and 3 in Table 1 illustrate that when the polyol is produced by the addition of ethylene oxide to methyliminobispropylamine (within formula (2) of the independent claims), superior curability is obtained relative to Comparative Examples 2 and 3 that use polyols produced by adding ethylene oxide to ethylene diamine, a common aliphatic amine compound that does not meet formula (2). It will also be noted that Comparative Example 4 uses Polyol J which is also prepared from methyliminobispropylamine, but which has an amine value and hydroxyl number outside of those claimed (see the discussion at the bottom of page 29) and provides inferior results.

With respect to Table 2, a comparison of Examples 5 and 6 shows that when the polyol is produced by adding ethylene oxide to methyliminobispropylamine

¹ Due to the length of the chapters, they have not been attached. However, at the request of the Examiner applicants will provide them.

(Example 5), superior results with respect to closed cell properties, elongation and wet heat compression set can be obtained relative to when the polyol is produced by adding ethylene oxide to 1-(2-aminoethyl)piperazine. Comparative Example 7 in Table 2 illustrates the adverse consequences of too much polyol (D) in the composition (i.e., 3.2%) while other Comparative Examples show the effect of too little polyol (D).

The WO '976 publication does not in any way disclose or teach the defined foam or composition which includes 0.5 to 3 parts by weight of the polyol (D) having the defined amine value and the defined hydroxyl value that is produced by the addition of an alkylene oxide to at least one amine compound represented by defined formula (II). It is noted that the WO '976 publication expressly distinguishes between flexible and rigid foams and in the paragraph bridging pages 8 and 9 states that in the production of "flexible polyurethane foam", the average hydroxyl number should be in the range of 20 to 100 mg KOH/g, preferably from 20 to 70 mg KOH/g. Therefore, it is clear that the WO '976 publication would actually teach away from this aspect of applicants' invention.

With regard to the recited amount of polyol (D) being 0.5 to 3 parts by weight, applicants again note that the evidence of record demonstrates the relevance of this recitation. In contrast, the WO '976 publication discloses that (b2) (the material alleged to meet polyol (D) in the Action) is present in an amount of 5 to 100 parts by weight. The illustrative materials of (b2) are Polyol B at page 22, line 30 having a 1,000 EW which corresponds to a hydroxyl value of 56 mg KOH/g and Polyol F on page 23, line 20 having a 1,700 EW that corresponds to a hydroxyl value of about 33 mg KOH/g. Furthermore, Polyol B is used in an amount of 100% in Table 1, 40 and

50% in Table II, 20, 40.4 and 20.2% in Table IV and 50% in Table VI while Polyol F is used in an amount of 95.5 and 46.75% in Table VII. Therefore, this information, which cannot be ignored, also would lead those of ordinary skill in the art away from the present invention.

Accordingly, without improperly resorting to applicants' own specification, the WO '976 publication would not lead those of ordinary skill in the art to applicants' claimed invention or to an appreciation of the substantial advantages which can be obtained therefrom. Indeed, by following the teachings of the WO '976 publication, one would be led away from invention as defined in the claims.

The further reliance on Falke et al., U.S. Patent No. 6,087,410, to show the wet heat compression set ratio and density recited in dependent claims 6 and 7 does not remedy the substantial shortcomings of the WO '976 publication. Thus, even assuming for the sake of argument that a proper basis exists for combining the documents in the manner advanced by the Examiner, the claims of record are still patentable over the combination of patent documents.

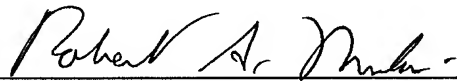
For all of the reasons set forth above, applicants respectfully submit that the claims of record are patentable over the cited prior art, especially in view of the technical evidence that has been provided, and therefore request reconsideration and allowance of the present application.

Should the Examiner have any questions concerning the subject application, the Examiner is invited to contact the undersigned attorney at the number provided below.

The Director is hereby authorized to charge any appropriate fees under 37 C.F.R. §§ 1.16, 1.17 and 1.20(d) and 1.21 that may be required by this paper, and to credit any overpayment, to Deposit Account No. 02-4800.

Respectfully submitted,

BUCHANAN INGERSOLL & ROONEY PC

By: 
Robert G. Mukai
Registration No. 28,531

Customer No. 21839
703 836 6620

Date: September 3, 2010

Polyurethane Handbook

Chemistry – Raw Materials – Processing –
Application – Properties

Edited by Dr. Günter Oertel

With 544 Figures and 121 Tables

With contributions from

L. Abele, Dr. A. Awater, H. Boden, Dr. F.-K. Brochhagen, Dr. M. Dahm,
Dr. D. Dietrich, Dr. W. Dietrich, Prof. Dr. W. Diller, Dr. M. Dollhausen,
Dr. F. Ehrhard, Dr. H.-A. Freitag, G. Gabrysch, Dr. H. Gall, Dr. W. Goyert,
Prof. Dr. E. Grigat, Dr. W. Hahn, Dr. G. Hauptmann, Dr. H. Hespe,
Dr. R. Hirtz, J. Hoffmann, H.-G. Hoppe, Dr. W. Kallert, Dr. H. Kleinmann,
Dr. U. Kuipp, Dr. H. J. Koch, Dr. K.-J. Kraft, B. Krüger, Dr. R. Kubens,
Dr. G. Loew, Dr. E. Meisert†, Dr. G. Mennicken, Dr. F. Müller, H. Ostrowski,
F. Prager, Dr. K. Recker, Dr. M. Roegner, Dr. H. M. Rotharmel,
Dr. H.-D. Ruprecht, H.-I. Sachs, Dr. H. Schäfer, Dr. K. Schauerte,
Dr. H.-G. Schneider, K. Schulte, Dr. K. Seel, Dr. H. Thomas, Dr. H. Toepsch,
Dr. H. Träubel, Dr. K. Uhlig, Dr. J. Vogel, Dr. R. Volland, U. Walber,
Dr. Ch. Weber, Dr. W. Wellner, H. Wieszorek, Dr. H. Wirtz,
Dr. K.-H. Wolf, Dr. R. Zöllner



Hanser Publishers, Munich Vienna New York

Distributed in the United States of America by
Macmillan Publishing Co., Inc., New York
and in Canada by
Collier Macmillan Canada, Ltd., Toronto

Numerical flammability ratings mentioned in this book are not intended to reflect hazards presented by those or any other materials under actual fire conditions.

Edited by
Dr. Günter Oertel
Bayer AG, PU Anwendungstechnik
D-5090 Leverkusen, Bayerwerk

Published by
Carl Hanser Verlag
Kolbengasse 22
D-8000 München 80

Distributed in USA by
Scientific and Technical Books
Macmillan Publishing Co., Inc.
866 Third Avenue, New York, N. Y. 10022

Distributed in Canada and Latin America by
Collier Macmillan International
866 Third Avenue, New York, N. Y. 10022-6299

Distributed in the United Kingdom by
Adam Hilger Ltd.
Techno House, Redcliffe Way
Bristol BS1 1, 6MX Great Britain

Distributed in all other countries via
Carl Hanser Verlag
Kolbengasse 22
D-8000 München 80

CIP-Kurztitelaufnahme der Deutschen Bibliothek

Polyurethane Handbook: Chemistry - Raw Materials -
Processing - Applications / ed. by Günter Oertel.
With contributions from L. Abele ... - Munich ;
Vienna : New York : Hanser, 1985.
Einheitsacht. : Polyurethane <engl.>
Teilung von: Kunststoff-Handbuch
ISBN 3-446-13671-1

NE: Oertel, Günter [Hrsg.] ; Abele, Lothar [Mitverf.] ;
EST

ISBN 0-02-948920-2 Macmillan Publishing Co., Inc., New York
Library of Congress Catalog Card Number 85-060442

All rights reserved. No part of this book may be reproduced or transmitted in any form or by any means, electronic or mechanical, including photocopying, recording or by any information storage and retrieval system, without permission from the publisher.

Copyright © Carl Hanser Verlag, Munich 1985

Printed in Germany (FRG) by Spandau-Druck GmbH, Nürnberg

Preface

The "Polyurethanes" volume of the Kunststoff-Handbuch series was selected for translation into English in light of the tremendous pace of technological development and commercial progress since the basic invention of polyurethane chemistry by Prof. Otto Bayer nearly 50 years ago.

Today, numerous building blocks and polymer structures are available to chemists and engineers for the synthesis of polyurethanes by the polyaddition principle. During fifty years of polyurethane chemistry, several polyisocyanates have become available on a technical scale. Most prominent and important among them are the two high volume product groups: toluene diisocyanate (TDI) and diphenyl methane diisocyanate (MDI). Using isocyanates and a multitude of polyester- and polyether-polyols, the polyurethane chemist was able to tailor make thermoset and thermoplastic materials. Understanding the dependence of physical properties on polymer morphology is an invaluable tool in this process. Progress in polymer physics and in polymer analysis has made special contributions towards that understanding.

Because the manufacturer of polyurethane articles converts low-molecular weight raw materials into finished polymers at the production site, we have placed special emphasis on the chemistry of polyurethane raw materials, on process description, and on processing equipment. We sincerely thank the authors of this volume for their efforts. Special thanks go to Mrs. Petra Böckly, as well as to Drs. Brochhausen, Hahn, Rothermel, Schauerle and Uhlir, who integrated the various chapters and formulated the final version of the book.

This volume was not translated by professional translators, but by experts in polyurethane technology at the Mobay Chemical Corporation under the supervision of Dr. J. Ick. We thank the translating team for their effort, and hope that the technical quality of the English edition compensates for any possible stylistic flaws.

Leverkusen, April 1985

Günter Oertel

Contents

1 Polyurethanes and their Market (<i>Dr. R. Hirtz, Dr. K. Uhlig</i>)	1
1.1 The Development of the Polyurethanes	1
1.2 The Market of the Polyurethanes	2
Reference list for Chapter 1	6
2 Chemical and Physical-Chemical Principles of Polyurethane Chemistry (<i>Dr. D. Dieterich, Prof. Dr. E. Grigat, Dr. W. Hahn</i>)	7
2.1 Chemical Principles (<i>Prof. Dr. E. Grigat</i>)	7
2.1.1 Basic reactions of the isocyanate group	7
2.1.1.1 Addition of nucleophilic reactants	8
2.1.1.2 Self-addition reactions of isocyanates	9
2.1.2 Formation of polyurethanes	11
2.2 Important Building Blocks for Polyurethanes (<i>Dr. W. Hahn</i>)	12
2.2.1 Isocyanates	12
2.2.2 Polyols	16
2.2.3 Diamines	18
2.2.4 Additives	19
2.3 Preparation Methods for Polyurethanes (<i>Dr. D. Dieterich</i>)	19
2.3.1 Solvent-free reactions	19
2.3.1.1 One-shot process	19
2.3.1.2 Prepolymer process	20
2.3.2 Reactions in solution	21
2.3.2.1 Completely reacted one-component systems	21
2.3.2.2 Reactive one-component systems	22
2.3.2.3 Two-component systems	22
2.3.3 Aqueous two-phase systems	22
2.4 Recent Developments (<i>Dr. D. Dieterich</i>)	24
2.4.1 Aqueous polyurethane dispersions	24
2.4.1.1 Emulsifier-containing dispersions	24
2.4.1.2 Ionomer dispersions	24
2.4.1.3 Non-ionic dispersions	26
2.4.1.4 Properties of dispersions	26
2.4.2 Powders	26
2.4.3 Microcapsules	27
2.4.4 Hydrogels	27
2.4.5 Aqueous solutions	28
2.4.6 Poromerics	28
2.4.7 Medical applications	28
2.4.7.1 Applications for external use	28
2.4.7.2 Artificial organs	29
2.4.8 Matrix foams	29
2.4.9 Organo-mineral systems	29
2.4.10 Mixtures with other polymers	30
2.5 Perceptions on the physical chemistry of the structure of polyurethanes (<i>Dr. D. Dieterich in cooperation with Dr. H. Hespe</i>)	31

2.5.1 Two-component polyurethanes without segmented structure	31
2.5.2 Segmented polyurethanes	32
2.5.2.1 Hard and soft segments	32
2.5.2.2 Segregation and domain morphology	33
2.5.2.3 Morphology within the hard segment domains	34
2.5.2.4 Effects of hard segments domains on mechanical and thermal properties	35
2.5.2.5 The effect of the soft segment matrix on thermal and mechanical properties	36
2.5.2.6 Crosslinked polyurethanes	37
2.5.3 Ionomers	38
Reference list for Chapter 2	39
3 Raw Materials	
(Dr. K. Schaefer in cooperation with Dr. M. Dahm, Prof. Dr. W. Diller, Dr. K. Uhlig)	
3.0 Introduction (Dr. K. Schaefer)	42
3.1 Polyols (Dr. K. Schaefer)	42
3.1.1 Polyether	42
3.1.1.1 Chemical structure	44
3.1.1.2 Raw materials for polyethers	45
3.1.1.3 Commercial production	47
3.1.1.4 Typical properties	49
3.1.1.5 Transport, storage, handling	50
3.1.1.6 Quality and analysis	52
3.1.1.7 Commercial products	53
3.1.2 Polyester	54
3.1.2.1 Chemical structure	54
3.1.2.2 Raw materials for polyesters	56
3.1.2.3 Commercial production	56
3.1.2.4 Properties	57
3.1.2.5 Transportation, storage, handling	59
3.1.2.6 Quality and analysis	60
3.1.2.7 Commercial products	60
Reference list for Chapter 3.1	60
3.2 Isocyanates (Dr. K. Schaefer)	62
3.2.1 Reaction Characteristics	63
3.2.2 Starting Materials for Isocyanates	63
3.2.3 Commercial production	65
3.2.3.1 Chemical background	65
3.2.3.2 Phosgenation processes	66
3.2.3.3 Product processing	67
3.2.3.4 Special manufacturing processes	68
3.2.4 Characteristics	68
3.2.5 Transportation, storage, and handling	70
3.2.6 Quality and analysis	72
3.2.7 Commercial products	72
Reference list for Chapter 3.2	72
3.3 Conversion Products of Raw Materials (Dr. K. Schaefer)	74
3.3.1 Conversion products of polyols	74

3.3.1.1 Filled polyols	75
3.3.1.2 Polyol prepolymer	76
3.3.1.3 Storage, transport, handling	76
3.3.2 Conversion products of polyisocyanates	77
3.3.2.1 Low-molecular weight urethane polyisocyanates	77
3.3.2.2 Polyisocyanates with uretidion, isocyanurate, and carbodiimide groups	79
3.3.2.3 Polyisocyanates with allophanate, urea, and biuret groups	81
3.3.2.4 Polyisocyanate prepolymer	82
3.3.2.5 Blocked polyisocyanates	83
3.3.2.6 Fatty acid-modified isocyanates	85
3.3.2.7 Transport, storage, handling	85
3.3.3 High-molecular weight polyurethane-polyols	86
3.3.3.1 Solid materials	86
3.3.3.2 Solutions of solid materials	88
3.3.3.3 Polyurethane polyols produced in solution	88
3.3.3.4 Solid materials from solutions	88
3.3.3.5 Transport, storage, handling	89
Reference list for Chapter 3.3	89
3.4 Additives and Auxiliary Materials (Dr. M. Dahm, Dr. K. Uhlig)	90
3.4.1 Catalysts	90
3.4.1.1 Terms of reaction kinetics	91
3.4.1.2 Catalysts for NCO/NCO-reactions	94
3.4.1.3 Catalysts for the NCO/OH-reaction	95
3.4.2 Inhibitors	96
3.4.3 Cross-linkers/chain extenders	97
3.4.3.1 Alcohols	97
3.4.3.2 Amines	98
3.4.3.3 Special cross-linking principals	98
3.4.4 Surfactants	98
3.4.4.1 Emulsifiers	98
3.4.4.2 Foam stabilizers	99
3.4.4.3 Cell regulators	100
3.4.5 Blowing agents	101
3.4.5.1 Chemical blowing procedure	101
3.4.5.2 Physical blowing procedures	101
3.4.6 Additives for flame retardance	102
3.4.7 Fillers	103
3.4.8 Antiaging agents	104
3.4.9 Mold release agents	105
3.4.10 Biocide addition agents	105
3.4.11 Coloring agents and coloring	105
3.4.12 Special additives	106
3.4.13 Handling, storage, transport	106
Reference list for Chapter 3.4	108
3.5 Industrial Hygiene of PU Raw Materials (Prof. Dr. W. F. Diller)	110
3.5.1 Polypols and polyol formulations	110
3.5.2 Isocyanates	110
3.5.2.1 Acute effects of isocyanates	111
3.5.2.2 Chronic exposure to isocyanate	112
3.5.2.3 Protective medical measures	113

3.5.3 Additives	114
3.5.3.1 Catalysts	114
3.5.3.2 Crosslinkers	115
3.5.3.3 Blowing agents and solvents	115
3.5.3.4 Other additives	116
Reference list for Chapter 3.5	
4 Polyurethane Processing (H. Boden, K. Schulte, Dr. H. Wirtz)	117
4.1 Basics	117
4.2 Design Principles for Polyurethane Processing Equipment	120
4.2.1 Comparison of the metering and mixing machine systems	120
4.2.2 Comparison of the plant systems	124
4.3 Steps of the Polyurethane Processing	129
4.3.1 Delivery and storage of the raw materials	129
4.3.2 Preparation of components	131
4.3.3 Metering	134
4.3.4 Mixing	143
4.3.5 Pouring	152
4.3.6 Process Controls	156
Reference list for Chapter 4	159

5 Flexible Foams

(Dr. H. A. Freitag, Dr. G. Hauptmann, Dr. K. Recker, Dr. M. Roegler, Dr. H. Schäfer, Dr. R. Volland)

5.0 Introduction (Dr. G. Hauptmann)	161
5.1 Slabstock Foams (Dr. M. Roegler)	162
5.1.1 Production of slabstock foams	163
5.1.1.1 Machines for the production of slabstock foams	165
5.1.1.2 Process description	169
5.1.1.3 Curing and storing of slabstock foams	171
5.1.1.4 Fabrication of slabstock foams	176
5.1.1.5 Utilization of cutting scrap	177
5.1.1.6 Slab foam systems and their manufacturing formulations	184
5.1.2 Properties of slabstock foams	192
5.1.3 Applications for slabstock foams	192
5.1.3.1 Furniture cushioning	193
5.1.3.2 Mattresses	194
5.1.3.3 Transportation	194
5.1.3.4 Textile foams	194
5.1.3.5 Packaging	195
5.1.3.6 Household goods	196
5.1.3.7 Miscellaneous application	198
5.2 Carpet Backing (Dr. K. Recker)	198
5.2.1 Products for backing	198
5.2.2 Production	198
5.2.2.1 Reverse coating	199
5.2.2.2 Direct coating	199

5.2.3 Properties	200
5.3 Flexible Polyurethane Molded Foam (Dr. H.-A. Freitag, Dr. A. Volland)	201
5.3.1 Production of flexible molded foams	201
5.3.1.1 Raw materials	206
5.3.1.2 Process technology	212
5.3.2 Properties of molded foams	218
5.3.3 Applications of molded flexible foam	223
5.4 Semi-Rigid Polyurethane Molded Foams (Dr. H. Schäfer)	223
5.4.1 Production	223
5.4.1.1 Raw materials and production methods	224
5.4.1.2 Processing technology	228
5.4.2 Properties	228
5.4.2.1 Mechanical properties	229
5.4.2.2 Damping properties	230
5.4.3 Applications	230
5.4.3.1 Protective padding	230
5.4.3.2 Foamed cavities	231
5.4.3.3 Energy management foams	231
5.4.3.4 Floor mats	231
5.4.3.5 Miscellaneous applications	231
Reference list for Chapter 5	232

6 PU Rigid Foam

(Dr. F.-K. Brochhagen, Dr. W. Dietrich, G. Gabrysich, Dr. K. J. Kraft, Dr. R. Kubens, Dr. G. Loew, Dr. K. Zellner)

6.0 Introduction (Dr. K. J. Kraft)	234
6.1 Chemistry and Raw Materials (Dr. W. Dietrich)	235
6.1.1 Polyols	235
6.1.2 Polyisocyanates	237
6.1.3 Blowing agents and other additives	238
6.2 Manufacturing of Rigid Polyurethane Foams (G. Gabrysich)	238
6.2.1 Manufacturing of buns	239
6.2.2 Continuous production of panels	239
6.2.2.1 Insulation panels	240
6.2.2.2 Laminated panels with metal surfaces	240
6.2.2.3 Composite panels	240
6.2.3 Discontinuous production of panels	240
6.2.3.1 Shell method	240
6.2.3.2 Foam filling technique	242
6.2.3.3 Fillers	243
6.2.4 Foaming of appliances	243
6.2.4.1 Refrigerator/freezer cabinets	244
6.2.4.1.1 Assembly lines with movable fixtures	245
6.2.4.1.2 Installations with stationary fixtures	245
6.2.4.2 Refrigerator and freezer doors	246
6.2.4.3 Water heaters	246
6.2.5 Processing of pre-insulated pipes	247
6.2.6 Pipe shells	247
6.2.7 PU in situ foam	247

6.2.7.1 Two-component in situ foam	247
6.2.7.2 Pressurized container system	248
6.3 Properties of PU Rigid Foam (Dr. R. Zöllner)	249
6.3.1 General	249
6.3.1.1 Isotropy — Anisotropy	249
6.3.1.2 Test samples for property determination	250
6.3.1.3 Cell structure	250
6.3.2 Mechanical properties	250
6.3.2.1 Compressive strength	251
6.3.2.2 Tensile strength	252
6.3.2.3 Bending and shear strength	252
6.3.2.4 Effect of heat and time on properties	253
6.3.3 Dimensional stability at low and high temperature	254
6.3.4 Open cells — Closed cells	254
6.3.5 Thermal conductivity	255
6.3.5.1 Effect of density	255
6.3.5.2 Effect of the cell gas	255
6.3.5.3 Effect of temperature	257
6.3.5.4 Effect of moisture	257
6.3.6 Water absorption	257
6.3.7 Thermal coefficient of expansion	258
6.3.8 Chemical resistance	258
6.3.9 Combustibility	259
6.4 Relationship between Production Methods and Properties (Dr. W. Dietrich, Dr. R. Zöllner)	260
6.4.1 Slabstock foam and continuously produced laminated boards	260
6.4.1.1 Slabstock foam	261
6.4.1.2 Continuously produced laminated boards with facers	261
6.4.1.2.1 Flexible facers	262
6.4.1.2.2 Rigid facers on one side	263
6.4.1.2.3 Rigid facers on both sides	266
6.4.2 Discontinuously produced PU sandwich elements	268
6.4.3 Molded parts with facers	269
6.4.3.1 Appliances	270
6.4.3.2 Preinsulated pipes for district heating	271
6.4.4 Pour-in-place rigid urethane foam	273
6.5 Application of Rigid PU Foams (Dr. G. Loew)	273
6.5.1 Refrigeration technology and appliances	273
6.5.1.1 Refrigerators and freezers	274
6.5.1.2 Commercial display cases	274
6.5.1.3 Refrigerated trucks and containers	275
6.5.1.4 Refrigerated warehouses and walk-in-coolers	276
6.5.1.5 Water heaters	277
6.5.2 Construction industry	277
6.5.2.1 Insulation boards	285
6.5.2.2 Sandwich elements	288
6.5.2.3 Specialty elements	290
6.5.2.4 PU lightweight concrete	290
6.5.2.5 Wall blocks with integrated insulation	292
6.5.2.6 Spray foam	292
6.5.2.7 One-component foam from pressurized containers	295

6.5.3 Technical insulation	296
6.5.3.1 Pipe insulation	296
6.5.3.1.1 Half-shells and moldings	296
6.5.3.1.2 Preinsulated pipes	297
6.5.3.1.3 Pour-in-place foam	298
6.5.3.2 Insulation of tanks	299
6.5.3.2.1 Normal temperature range	300
6.5.3.2.2 Low temperature range	301
6.5.4 Automotive industry	301
6.5.4.1 Interior liners	303
6.5.4.2 Cavity foaming	304
6.5.5 Transportation	304
6.5.5.1 Refrigerated vehicles	305
6.5.5.2 Insulation for transportation of special products	305
6.5.5.3 Caravans and mobile homes	305
6.5.6 Shipbuilding	305
6.5.6.1 Foaming of cavities	305
6.5.6.2 Insulation of cold storage holds in fishing boats	306
6.5.6.3 Boat building	306
6.5.7 Packaging	306
6.5.7.1 Direct encapsulation	308
6.5.7.2 Transportation protection in vehicles	308
6.5.7.3 Sandwich-Cardboard Boxes	309
6.5.8 Other fields of application	309
6.5.8.1 Rigid polyurethane foams for horticulture	311
6.5.8.2 Sporting goods	311
6.5.8.3 Furniture	311
6.5.8.4 Solar technology	312
6.5.8.5 "Radomes"	312
6.6 Consolidation of Coal and Surrounding Strata (Dr. R. Kubens)	312
6.6.1 The cartridge process	313
6.6.1.2 Injection process	313
Reference list for Chapter 6	314
7 Polyurethane Integral Skin Foam (Dr. H. Kleinmann, Dr. U. Kripp, Dr. E. Meisert†, Dr. H. Schäfer, Dr. H.-G. Schneider, Dr. K. Seel, Dr. H. Thomas, Dr. Ch. Weber, Dr. H. Wirtz)	315
7.1 Introduction (Dr. H. Wirtz)	315
7.2 Production Technology (Dr. U. Kripp)	318
7.2.1 Metering and mixing technique	318
7.2.2 Gating and molds	318
7.2.2.1 Gating	320
7.2.2.2 Molds	323
7.2.3 Mold carriers	325
7.3 Flexible Polyurethane Integral Skin Foams	325
7.3.1 Polyether foams (Dr. Ch. Weber)	325
7.3.1.1 Manufacturing	326
7.3.1.2 Properties	333
7.3.2 Flexible polyester foams (Dr. E. Meisert†)	333

8.2.2.7 Calendaring	411
8.2.2.8 Bonding/Welding	411
8.2.3 Properties (Dr. W. Goyert)	412
8.2.3.1 Heat resistance	412
8.2.3.2 Low temperature behavior	414
8.2.3.3 Dynamic characteristics	415
8.2.3.4 Gas permeability	415
8.2.3.5 Chemical resistance	416
8.3 Special Elastomers	418
8.3.1.3 Millable urethane gum (Dr. W. Kallert)	418
8.3.1.1 Production	418
8.3.1.2 Vulcanization systems	419
8.3.1.3 Particulars for processing	421
8.3.1.4 Properties of the vulcanizate	421
8.3.1.5 Water crosslinking	422
8.3.2 Polyurethane prepolymers (Dr. K. Recker)	422
8.3.2.1 Production	422
8.3.2.2 Processing of polyurethane prepolymers	423
8.3.2.3 Properties	423
8.4 Applications for Polyurethane Elastomers (H.-G. Hoppe)	424
8.4.1 Applications in the automobile sector	426
8.4.1.1 Wheel joints, tie rod joints, axle strut joints	426
8.4.1.2 Hydro pneumatic suspension system	427
8.4.1.3 Supplementary spring from cellular PU elastomers	428
8.4.1.4 Exterior auto body parts	429
8.4.1.5 Polyurethane cast tires	430
8.4.2 General engineering applications	430
8.4.2.1 Rollers and roll covers	430
8.4.2.2 Milling rolls	432
8.4.2.3 Damping elements	433
8.4.2.4 Drive components	435
8.4.2.5 Wear resistant elements	437
8.4.2.6 Gaskets	438
8.4.3 Applications in the construction industry	438
8.4.3.1 Sport and track surfaces	439
8.4.3.2 Terra cotta pipe seals	440
8.4.3.3 Formwork mats	441
8.4.4 Applications in the electrical area	442
8.4.5 Applications for the shoe industry	443
8.4.5.1 Shoe outside covers	444
8.4.5.2 Sport shoe soles	445
8.4.6 Films and tubes	445
8.4.6.1 Films	445
8.4.6.2 Tubes	447
Reference list for Chapter 8	447

9 Determination of the Composition and Properties of Polyurethanes

(J. Hoffmann, H. Ostrow, F. Prager, Dr. H. M. Rothmel, Dr. J. Vogel)	450
9.0 Introduction (Dr. H. M. Rothmel)	450
9.1 Determination of the Chemical Composition (H. Ostrow, Dr. J. Vogel)	450

7.3.2.1 Production	333
7.3.2.2 Properties	333
7.3.3 Part production (Dr. H. Schäfer)	335
7.3.3.1 Test sheets	335
7.3.3.2 Parts	336
7.3.3.3 Release agents	336
7.3.3.4 Post-finishing	337
7.3.3.5 Coloring	337
7.3.4 Applications of flexible integral foams (Dr. H. Schäfer, Dr. H. Thomas)	338
7.3.4.1 Automotive and other technical applications	338
7.3.4.2 Shoe industry	342
7.4 Rigid PU Integral Skin Foam	346
7.4.1 Preparation (Dr. U. Knipp)	346
7.4.2 Properties (Dr. H. Kleinmann)	347
7.4.3 Finishing (Dr. H. Kleinmann)	355
7.4.4 Applications (Dr. H.-G. Schneider)	357
7.5 Reinforced PU Integral Skin Foams (Dr. K. Seel)	362
7.5.1 Production	362
7.5.2 The influence of fillers and reinforcing materials on the physical of PU integral skin foams	364
7.5.3 Applications	369
Reference list for Chapter 7	369

8 Solide Polyurethane Materials

(Dr. A. Awater, Dr. F. Ehrhard, Dr. W. Goyert, H.-G. Hoppe, Dr. W. Kallert, Dr. K. J. Kraft, B. Krüger, Dr. K. Recker, Dr. K. Schauterte, Dr. W. Wellner)	371
8.0 Introduction (Dr. K. J. Kraft)	371
8.1 PU Casting Systems	372
8.1.1 PU cast elastomers (Dr. A. Awater)	374
8.1.1.1 Raw materials	374
8.1.1.2 Dewatering of the polyol	376
8.1.1.3 Hot cure systems, production and processing	381
8.1.1.4 Polyurethane cold cure systems	383
8.1.1.5 Reactive spray coatings	383
8.1.1.6 Properties of polyurethane cast elastomers	388
8.1.2 Casting Resins	388
8.1.2.1 Electrical Sector (Dr. F. Ehrhard)	402
8.1.2.2 Joint sealants (Dr. W. Wellner)	405
8.2 Thermoplastic Polyurethane Elastomers	406
8.2.1 Production (Dr. W. Goyert)	406
8.2.1.1 Laboratory preparation	406
8.2.1.2 Technical production	407
8.2.1.3 Mixtures with other materials	407
8.2.2 Processing (B. Krüger)	407
8.2.2.1 Preparation of the pellets	407
8.2.2.2 Post-treatment of the finished parts	407
8.2.2.3 Use of scrap and regrind	408
8.2.2.4 Addition of colorants	408
8.2.2.5 Injection molding	410
8.2.2.6 Extrusion	410

9.1.1 Detection methods and elucidation procedures	450
9.1.1.1 Chemical detection methods	450
9.1.1.2 Thin layer chromatography	451
9.1.1.3 Gas chromatographic methods	451
9.1.1.4 Infrared spectroscopy	451
9.1.1.5 Nuclear magnetic resonance spectrometry	451
9.1.1.6 Hydrolytic methods	451
9.1.2 Identification of functional groups	452
9.1.2.1 Isocyanates	452
9.1.2.2 Residual NCO groups	453
9.1.2.3 Determination of free monomeric isocyanates	453
9.1.2.4 Polyesters	454
9.1.2.5 Polyethers	454
9.1.2.6 Differentiation between polyether and polyester urethanes	454
9.1.2.7 Chain extenders	455
9.1.2.8 Auxiliaries and additives	455
9.2 Determination of Material Properties (<i>Dr. H. M. Rathmel</i>)	455
9.2.1 Standardized test methods	456
9.2.2 Test specimen preparation	461
9.2.3 Determination of linear dimensions	462
9.2.4 Determination of density/Apparent density	462
9.2.5 Determination of the cell structure	463
9.2.6 Determination of the fraction of open and closed cells in foams	464
9.2.7 Determination of the mechanical properties in short term experiments	465
9.2.7.1 Tensile experiments	465
9.2.7.2 Tear experiments	466
9.2.7.3 Compression experiments	467
9.2.7.4 Hardness determination	468
9.2.7.5 Flexural experiments	469
9.2.7.6 Shear experiments	469
9.2.7.7 Determination of the modulus of elasticity	470
9.2.7.8 Short duration experiments on core compounds	470
9.2.7.9 Impact experiments	471
9.2.8 Determination of the mechanical properties in long-term experiments under static load or constant deformation	473
9.2.8.1 Creep experiments	473
9.2.8.2 Compression set/tensile set	474
9.2.9 Determination of the mechanical properties under periodically varying load of deformation	475
9.2.9.1 Dynamic fatigue experiments on rigid integral skin foams	475
9.2.9.2 Dynamic fatigue experiment on flexible foams	475
9.2.9.3 Continuous bending experiments	475
9.2.10 Determination of the temperature dependence of properties	476
9.2.10.1 Determination of thermal expansion	476
9.2.10.2 Determination of the temperature dependence of characteristic values	476
9.2.10.3 Short duration experiments at various temperatures	478
9.2.10.4 Determination of the softening temperature	478
9.2.10.5 Dimensional stability in heat and cold	479
9.2.10.6 Creep pressure experiments as a function of temperature	480
9.2.11 Investigation of aging performance	480

9.2.11.1 Light and weather exposure	480
9.2.11.2 Determination of the stability against gases, liquids, and solids	481
9.2.12 Determination of friction and abrasion performance	481
9.2.13 Determination of the thermal conductivity rating	482
9.2.14 Determination of water vapor permeability	483
9.2.15 Determination of water uptake	484
9.2.16 Determination of the acoustical properties	484
9.2.17 Determination of electrical and dielectric properties	485
9.3 Suitability Determination through End-Product Testing (<i>J. Hoffmann</i>)	486
9.3.1 Simulation of day-to-day use	487
9.3.2 Measurement methods for end-product testing	488
9.3.2.1 Dimensional stability, determination of part weights and dimensions	488
9.3.2.2 Mechanical requirements	488
9.3.3 Examples of end-product testing	489
9.3.3.1 Testing of PU shoe soles	489
9.3.3.2 Testing of automobile seats	490
9.3.3.3 Experiments on bumper systems of automobiles	491
9.3.3.4 Automobile headliners	493
9.3.3.5 District heating systems	494
9.4 Combustibility Testing and Rating (<i>F. Prager</i>)	495
9.4.1 Generally used laboratory procedures	495
9.4.2 Mining applications	497
9.4.3 Electric applications	497
9.4.4 Transportation applications area	498
9.4.5 Furniture and furnishing	500
9.4.6 Construction applications areas	500
9.4.6.1 Construction materials	500
9.4.6.2 Construction elements and special constructions	503
9.4.7 Other fire-related factors	505
Reference list for Chapter 9	507

10 PU Paints and Coatings

(<i>Dr. H. Koch, Dr. G. Mennicken, Dr. F. Müller, Dr. H. Toepesch, Dr. H. Träubel, W. Wietzorek</i>)	510
10.1 Paints and Coatings (<i>Dr. G. Mennicken, W. Wietzorek</i>)	510
10.1.1 Solvent-containing, ambient-cure reactive coatings	511
10.1.1.1 Two-component PU coatings	511
10.1.1.2 One-component PU coating formulation	514
10.1.1.3 Manufacturing	515
10.1.1.4 Processing	515
10.1.1.5 Properties of the coating	517
10.1.1.6 Application areas	519
10.1.2 Solvent-borne non-reactive polyurethanes	520
10.1.3 Solvent-borne, air-dry coatings	521
10.1.4 Solvent-borne one-component storing lacquers	522
10.1.5 Solvent-free paints and coatings	525
10.1.5.1 Two-component coating	525
10.1.5.2 One-component coatings, moisture curing	526
10.1.5.3 PU modified epoxy systems	527

10.1.5.4 Oven-dried, solvent-free coatings	527
10.1.6 PU powder coatings	527
10.1.7 Industrial hygiene precautions for the use of PU coatings	529
10.2 Polyurethanes for Textile, Paper and Leather Coating (Dr. H. Träubel, Dr. H. J. Koch, Dr. H. Toepesch, Dr. F. Müller)	530
10.2.1 Textile application	530
10.2.1.1 Textile treatment (sizing)	530
10.2.1.2 Textile coating	531
10.2.1.2.1 Selection of the textile substrate	531
10.2.1.2.2 The polymer structure of the PU-products	532
10.2.1.2.3 Coating processes	533
10.2.1.2.4 Finishing of PU-coatings	534
10.2.1.3 Nonwoven bonding	534
10.2.1.4 Poromeric-imitation leather	534
10.2.1.4.1 Polyaddition using dispersions	536
10.2.1.4.2 Polyaddition in solution	537
10.2.1.4.3 The use for poromeric imitation leather	538
10.2.2 Paper	538
10.2.2.1 Polyurethane ionic dispersions for paper coating	538
10.2.2.1.1 Properties of polyurethane films	539
10.2.2.1.2 Working with polyurethane dispersions	539
10.2.2.1.3 Applications for food packaging paper	540
10.2.2.1.4 Other applications of polyurethane dispersions for paper coating	541
10.2.2.2 Polyurethane dispersions and solutions for paper sizing	541
10.2.3 Leather	542
10.2.3.1 Applications in tanning, retanning, coloring	542
10.2.3.2 Finishing	543
10.2.3.2.1 Impregnation and base coating of leather	543
10.2.3.2.2 Top finish	543
10.2.3.2.3 Patent leather	544
10.2.3.2.4 Foil finishing	544
10.2.3.3 Special processes	544
Reference list for Chapter 10	546

11 Polyurethane Adhesives

(Dr. M. Dollhausen)	548
11.1 Introduction	548
11.2 Polyisocyanates	548
11.3 Two-Component Reaction Adhesives	550
11.3.1 Polyisocyanates	550
11.3.2 Polyols	550
11.3.3 Auxiliaries	551
11.3.4 Production and processing	552
11.3.5 Adhesive bonds	553
11.4 One-Component Reaction Adhesives	553
11.4.1 Isocyanate terminated polyurethanes	554
11.5 Solvent Adhesives	554
11.5.1 Hydroxyl polyurethanes	554
11.5.2 Auxiliaries	555

11.5.3 Production and processing	555
11.5.4 Adhesive bonds	556
11.6 Dispersion Adhesives	557
11.6.1 Manufacturing	557
11.6.2 Auxiliaries	558
11.6.3 Processing	558
11.6.4 Adhesive bonds	558
11.7 Application Fields	559
11.7.1 Footwear industry	559
11.7.2 Bonding of plastics	560
11.7.3 Packaging applications	561
11.7.4 Clothing industry	561
11.7.5 Automotive industry	562
11.7.6 Building industry	562
Reference list for Chapter 11	562
12 Polyurethane (PU) and Isocyanates as Binders (Dr. K. J. Kraft, Dr. R. Kubens, Dr. K. Recker, Dr. H.-D. Rupprecht, H. I. Sachs)	563
12.0 Introduction (Dr. K. J. Kraft)	563
12.1 Bonding of Forest and Agricultural Products (H. I. Sachs)	564
12.1.1 The bonding of forest products	564
12.1.1.1 Manufacture	564
12.1.1.2 Properties	565
12.1.1.3 Applications	568
12.1.2 Bonding of agricultural products	569
12.1.2.1 Manufacture	569
12.1.2.2 Properties	569
12.1.2.3 Applications	570
12.2 Bonding of other Products (Dr. H.-D. Rupprecht, H. I. Sachs)	570
12.2.1 Rubber	570
12.2.1.1 Manufacture	570
12.2.1.2 Properties	570
12.2.1.3 Applications	570
12.2.2 Rigid polyurethane foam scrap	571
12.2.2.1 Manufacture	571
12.2.2.2 Properties	571
12.2.2.3 Applications	571
12.2.3 Inorganic products	572
12.2.3.1 Manufacture	572
12.2.3.2 Properties	572
12.2.3.3 Applications	572
12.3 Bonding of Foundry Sand (Dr. R. Kubens)	573
12.4 Sizing for Glass Fibers (Dr. K. Recker)	574
12.4.1 Manufacture	574
12.4.2 Properties	574
12.4.2.1 Processing properties	574
12.4.2.2 Properties of the glass fibers	575
12.4.2.3 Properties of the reinforced plastic	575
Reference list for Chapter 12	576

13 Polyurethane Elastomeric Fibers	577
(Dr. H. Gall, Dr. K.-H. Wolf)	
13.0 Introduction (Dr. H. Gall)	577
13.1 Synthesis of Segmented Polyurethanes (Dr. K.-H. Wolf)	577
13.1.1 Reactants	577
13.1.2 Reactions	578
13.1.2.1 Preparation of NCO prepolymers	578
13.1.2.2 Preparation of the elastane solution	579
13.1.2.3 Modifying reactions	579
13.1.3 Crosslinked elastanes	579
13.1.4 Additives	579
13.2 Spinning Processes (Dr. K.-H. Wolf)	580
13.2.1 Dry spinning processes	580
13.2.2 Wet spinning processes	581
13.2.3 Reaction spinning methods	581
13.2.4 Miscellaneous processes	581
13.2.5 Post treatments	581
13.2.6 Compounding	581
13.3 Physical Crosslinking of Segmented Polyurea — Urethane Elastomers	582
(Dr. K.-H. Wolf)	
13.3.1 Influence of hard segments	582
13.3.2 Influence of the soft segments	582
13.4 Properties and Testing of Elastane Yarns (Dr. H. Gall)	583
13.4.1 Mechanical properties	584
13.4.2 Thermal behavior	584
13.4.3 Chemical characteristics	585
13.4.4 Coloration	586
13.5 Manufacture and Operations (Dr. H. Gall)	586
13.5.1 Types of yarn	586
13.5.2 Production and application of elastic fabrics	587
13.5.2.1 Knit fabrics	587
13.5.2.2 Woven fabrics	589
13.5.3 Dyeing and finishing	589
13.5.4 Characteristics of elastane-containing fabrics	590
Reference list for Chapter 13	590
14 Polyurethane and the Environment	592
(L. Abele, Dr. F.-K. Brochhagen, U. Walber)	
14.0 Introduction (Dr. F.-K. Brochhagen)	592
14.1 Industrial Hygiene in Manufacturing and Processing (U. Walber)	593
14.1.1 Regulations and guidelines	593
14.1.2 Protective measures at the workplace	593
14.1.2.1 Solvent-free raw material systems — stationary processing	595
14.1.2.2 Solvent-free raw material systems — non-stationary processing	598
14.1.2.3 Processing solvent-containing systems	598
14.1.2.4 Processing polyurethanes	599
14.2 Ecology of Polyurethanes (L. Abele)	599
14.2.1 Emission into the atmosphere	599
14.2.2 Liquid and solid raw materials	600
14.2.3 Polyurethanes as waste product	601
14.2.3.1 Dumping	602
14.2.3.2 Incineration	602
14.2.3.3 Recycling	603
14.3 Polyurethanes as Foodstuffs-Commodities (Dr. F.-K. Brochhagen)	603
14.4 Flammability and Flammability Risk (Dr. F.-K. Brochhagen)	604
14.4.1 Flammability risks in the application	604
14.4.2 Flammability risks in production and storage	605
14.4.2.1 Polyurethane flexible foam in furniture and mattresses	605
14.4.2.2 Polyurethane foam in the transportation sector	606
14.4.2.3 Polyurethane in the building sector	606
14.4.3 Side effects of combustion	606
Reference list for Chapter 14	606
15 Commercial Products	608
(Dr. K. Uhlig)	
Index	619

Handbook of Polymeric Foams and Foam Technology

2nd Edition

Edited by

Daniel Klempner and Vahid Sendjarevic

With contributions by

R.M. Aseeva, K. Ashida, J.K. Backus, T. Baumann, R. Broos,
L. Domeier, C.V. Gupta, J.R. Harper, R. Herrington, P.T. Kelly,
D. Klempner, P. Knaub, R.F. Mausser, W. Nicholson, C.B. Park,
C.P. Park, J.H. Saunders, V. Sendjarevic, F.A. Shutov, K.W. Suh,
D. Visco, F. Xing

HANSER

Hanser Publishers, Munich

Hanser Gardener Publications, Inc., Cincinnati

Contributors List

Dr. Daniel Klemmner, University of Detroit Mercy, Polymer Institute, 4001 W. McNichols Road, Detroit, MI 48219-0900, USA
Dr. Valid Sendjarevic, Troy Polymers, Inc. 330 E. Maple Road, Troy, MI 48063, USA

Distributed in the USA and in Canada by
Hanser Gardner Publications, Inc.
6915 Valley Avenue, Cincinnati, Ohio 45244-3029, USA

Fax: (513) 527-5801
Phone: (513) 527-8977 or 1-800-950-8977
Internet: <http://www.hansergardner.com>

Distributed in all other countries by
Carl Hanser Verlag
Postfach 86 04 20, 81631 München, Germany
Fax: +49 (89) 98 12 64
Internet: <http://www.hanser.de>

The use of general descriptive names, trademarks, etc., in this publication, even if the former are not especially identified, is not to be taken as a sign that such names, as understood by the Trade Marks and Merchandise Marks Act, may accordingly be used freely by anyone.

While the advice and information in this book are believed to be true and accurate at the date of going to press, neither the authors nor the editors nor the publisher can accept any legal responsibility for any errors or omissions that may be made. The publisher makes no warranty, express or implied, with respect to the material contained herein.

Library of Congress Cataloging-in-Publication Data

Handbook of polymeric foams and foam technology / edited by Daniel Klemmner and Valid Sendjarevic ; with contributions by R. M. Aseeva ...
[et al.] -- 2nd ed.

p. cm.

ISBN 1-56990-336-0 (hardcover)

1. Plastic foams. I. Klemmner, Daniel. II. Sendjarevic, Valid. III.

Aseeva, R. M. (Roza Mikhaelovna)

TP1183.F6H36 2004

668.4'93--dc22

2003025345

Bibliografische Information Der Deutschen Bibliothek

Die Deutsche Bibliothek verzeichnet diese Publikation in der Deutschen Nationalbibliografie; detaillierte bibliographische Daten sind im Internet über <http://dnb.ddb.de> abrufbar.
ISBN 3-446-21831-9

All rights reserved. No part of this book may be reproduced or transmitted in any form or by any means, electronic or mechanical, including photocopying or by any information storage and retrieval system, without permission in writing from the publisher.

© Carl Hanser Verlag, Munich 2004
Production Management: Oswald Immler
Coverconcept: Mare Müller-Brenner, Reinbreitung, München, Germany
Coverdesign: MCP • Susanne Kraus GBR, Holzkirchen, Germany
Typeset, printed and bound by Kösel, Kempten, Germany

Kechang (Frank) Xing
Royal Group Technologies Ltd.
Woodbridge, ON, Canada

Chul B. Park
University of Toronto
Toronto, ON, Canada

Linda Domeier
Sandia National Laboratories
Albuquerque, NM

W. Nicholson
Dow Corning Corp.
Midland, MI

J.R. Harper
Dow Corning Corp.
Midland, MI

T. Baumann
Dow Corning Corp.
Midland, MI

C.V. Gupta
PolyChem Alloy, Inc.
Conover, NC

P.T. Kelly
Smithers Oasis Corp.
Kent, OH

Robert F. Mausser
Carter Products Research
Cranbury, NJ

R.M. Aseeva
Institute of Biochemical Physics, RAN
Moscow, Russia

Daniel Klemmner
University of Detroit Mercy
Detroit, MI

V. Sendjarevic
Troy Polymers, Inc.
Troy, MI

J.H. Saunders
Pensacola, FL

Fyodor A. Shurlov
Tennessee Technological University
Cookeville, TN

Donald Visco
Tennessee Technological University
Cookeville, TN

R. Herrington
Dow Chemical Co.
Freeport, TX

Rene Broos
Dow Chemical Co.
Freeport, TX

Philippe Knaub
Dow Chemical Co.
Freeport, TX

J.K. Backus
Allison Park, PA

Kaneyoshi Ashida
Farmington Hills, MI

K.W. Suh
Dow Chemical Co.
Midland, MI

Chung Poo Park
Dow Deutschland, Inc.
Rheinfelden, Germany

meric foams of all types. In addition, individuals engaged in marketing of foams or foam raw materials will find this book of practical value. It can also be used as a textbook for a course on polymeric foams.

The editors hope that this book will stimulate creative thinking and development of new technologies, types of foams, processes, and applications.

Daniel Klemperer
Yahid Scndjarevic

Acknowledgements

The editors wish to express their appreciation to the University of Detroit Mercy and to the staff of Troy Polymers, Inc. for their encouragement and helpful advice in this undertaking.

Contents

Preface.....	IX
1 Introduction.....	1
1.1 References.....	4
2 Fundamentals of Foam Formation.....	5
2.1 Introduction.....	5
2.2 Fundamental Principles of Foam Formation.....	6
2.2.1 Bubble Formation.....	6
2.2.2 Bubble Growth.....	8
2.2.3 Bubble Stability.....	9
2.3 Supporting Evidence from Specific Foam Systems.....	11
2.3.1 Thermoplastic Foams.....	11
2.3.2 Polyurethane Foams.....	12
2.3.3 Cellular Rubber.....	13
2.4 Summary.....	13
2.5 References.....	14
3 Cellular Structure and Properties of Foamed Polymers.....	17
3.1 Introduction.....	17
3.2 Porous and Cellular Systems.....	17
3.2.1 Statistical Meaning of the Concept of a Cell.....	17
3.2.2 Terminology.....	18
3.2.3 Basic Relationships.....	19
3.2.4 Packing Types.....	20
3.3 Open- and Closed-Cell Foamed Plastics.....	22
3.3.1 General Problems.....	22
3.3.2 Open Cells and Density.....	23
3.3.3 Reiculated Foams.....	24
3.4 Density of Foamed Polymers.....	24
3.4.1 Classification.....	24
3.4.2 Density and Cell Size.....	25
3.4.3 Density and Wall Thickness.....	26
3.5 Cell Shape of Foamed Polymers.....	28
3.5.1 Cell Shape Models.....	28
3.5.2 12- and 14-Hedrons.....	28
3.5.3 Anisotropy of Cell Shapes.....	30
3.6 Cell Size of Foamed Polymers.....	33
3.6.1 Methods of Estimation.....	33
3.6.2 Cell Size and Number of Cells.....	34
3.6.3 Cell Size and Wall Thickness.....	34
3.6.4 Microcells.....	35
3.6.5 Cell Size and Physical Properties.....	37
3.7 Models of Cellular Structure and Calculation of Mechanical Properties of Foamed Polymers.....	38

3.7.1 Flexible Foamed Polymers.....	38
3.7.2 Rigid Foamed Polymers.....	39
3.8 Cellular Structure and Thermal Conductivity of Foamed Polymers.....	40
3.8.1 Thermal Conductivity of the Polymer Phase.....	41
3.8.2 Thermal Conductivity of the Gas Phase.....	41
3.8.3 Radiative Thermal Conductivity.....	44
3.8.4 Convective Thermal Conductivity.....	45
3.8.5 Effects of Variables on the Thermal Conductivity.....	46
3.9 General Concepts.....	47
3.9.1 Three Generations of Polymer Foams.....	47
3.9.2 Six Structural Levels.....	48
3.9.3 Quantitative Parameters of Cellular Structure.....	49
3.9.4 Technological Concepts.....	50
3.9.5 Advantages of Foamed Polymers.....	51
3.10 References.....	52
4 Flexible Polyurethane Foams.....	55
4.1 Introduction.....	55
4.1.1 Applications.....	55
4.1.2 Markets.....	56
4.2 Basic Chemistry.....	57
4.2.1 The Polymerization Reaction.....	59
4.2.2 The Gas-Producing Reaction.....	60
4.2.3 Foam Recipe Components.....	61
4.3 Foam Morphology.....	77
4.3.1 Review of Current Concepts.....	77
4.3.2 Model for Flexible Foam Formation.....	84
4.4 Preparation of Flexible Foam.....	84
4.4.1 General Requirements.....	85
4.4.2 Laboratory-Scale Cup-Foaming.....	86
4.4.3 Laboratory Box-Foams.....	86
4.4.4 Machine-Made Foam.....	87
4.4.5 Mixing Heads.....	88
4.4.6 Commercial-Scale Processes.....	89
4.5 Foam Physical Properties.....	94
4.5.1 Foam Density.....	95
4.5.2 Load Bearing.....	95
4.5.3 Airflow.....	97
4.5.4 Cell Size.....	97
4.5.5 Compression Set.....	98
4.5.6 Tension Properties.....	99
4.5.7 Tear.....	99
4.5.8 Resilience.....	100
4.6 Slabstock Foams.....	100
4.6.1 Slabstock Chemistry.....	100
4.6.2 Alternative Blowing Agent Developments.....	100
4.6.3 High Load Bearing Foams.....	101
4.6.4 High Resilience Foams.....	102

4.6.5 Foam Flammability.....	102
4.6.6 Non-BHT Foams.....	103
4.6.7 Emulsions.....	104
4.6.8 Recycling.....	104
4.7 Molded Foam.....	105
4.7.1 Sealing Foams.....	105
4.7.2 Comfort.....	106
4.7.3 Durability.....	107
4.7.4 Fogging and Odor.....	108
4.8 References.....	109
5 Rigid Polyurethane Foams.....	121
5.1 Introduction.....	121
5.2 Structure.....	122
5.3 Chemistry.....	122
5.4 Reactants.....	123
5.4.1 Isocyanates.....	123
5.4.2 Polyols.....	124
5.4.3 Catalysts.....	125
5.4.4 Stabilizers.....	126
5.4.5 Blowing Agents.....	126
5.4.6 Combustion Modifiers.....	127
5.5 Formulations.....	127
5.6 Foam Preparation.....	128
5.6.1 Block and Sheet.....	129
5.6.2 Pour-in-Place.....	129
5.6.3 Spray.....	130
5.7 Foam Physics.....	130
5.8 Properties.....	131
5.8.1 Density.....	131
5.8.2 Mechanical Properties.....	131
5.8.3 Water, Solvent, and Chemical Resistance.....	132
5.8.4 Thermal Conductivity.....	132
5.8.5 Combustibility.....	134
5.9 Applications.....	136
5.10 Health and Safety.....	136
5.10.1 Isocyanates.....	137
5.10.2 Polyols.....	137
5.10.3 Catalysts.....	137
5.10.4 Blowing Agents.....	137
5.11 Future Trends.....	138
5.12 References.....	138
Acknowledgement.....	140
6 Polyisocyanurate Foams.....	141
6.1 Introduction.....	141
6.2 Isocyanurate Chemistry.....	143
6.2.1 Catalysts for Cyclotrimerization.....	143

6.2.2	Kinetics and Mechanisms of Cyclotrimerization	148
6.2.3	Relative Catalytic Activity	156
6.3	Preparation of Modified Polyisocyanurate Foams	160
6.3.1	Urethane-Modified Polyisocyanurate Foams	160
6.3.2	Oxazolidone-Modified Polyisocyanurate Foams	175
6.3.3	Amide-Modified Polyisocyanurate Foams	178
6.3.4	Carbodiimide-Modified Polyisocyanurate Foams	178
6.3.5	Imide-Modified Polyisocyanurate Foams	179
6.4	Applications	180
6.4.1	Composite Foam Boards	180
6.4.2	Flame-Retardant Seamless Insulation [61]	181
6.4.3	Building Insulation	182
6.4.4	Chemical and Petrochemical Plant Insulation	183
6.4.5	High-Rise Building Walls	183
6.4.6	Chemical-Resistant Floats	183
6.4.7	Cryogenic, Petrochemical, and Solar Energy Applications	183
6.4.8	Highly Resilient Flexible Polyurethane Foams	184
6.5	References	184
7	Polystyrene and Structural Foam	189
7.1	Introduction and General Description	189
7.1.1	Nomenclature	190
7.2	Chemistry and Preparation	190
7.2.1	Theory of the Expansion Process	191
7.2.2	Blowing Agent Selection	193
7.3	Properties and Their Relation to Structure	195
7.3.1	Test Methods	195
7.3.2	Properties of Commercial Products	195
7.3.3	Mechanical Properties	199
7.3.4	Thermal Properties	204
7.3.5	Moisture Resistance	206
7.3.6	Electrical Properties	207
7.3.7	Environmental Aging	207
7.3.8	Other Properties	207
7.4	Commercial Production and Processing	208
7.4.1	Manufacturing Process	208
7.4.2	Commercial Products and Processes	212
7.5	Applications	214
7.5.1	Cushioning	215
7.5.2	Thermal Insulation	216
7.5.3	Packaging	217
7.5.4	Structural Components	219
7.5.5	Marine Applications	219
7.5.6	Electrical Insulation	219
7.5.7	Space Filling and Seals	219
7.5.8	Other Uses	220
7.5.9	Energy Considerations in Foam Insulation	220

7.5.10	Health and Safety Factors	224
7.6	References	225
8	Polyolefin Foam	233
8.1	Introduction	233
8.2	Chemistry and Preparation	234
8.2.1	Foam Expansion with a Physical Blowing Agent	237
8.2.2	Foam Expansion with a Chemical Blowing Agent	248
8.3	Properties and Their Relation to Structure	262
8.3.1	Properties of Commercial Products	266
8.3.2	Relationships Between Structure and Properties	267
8.4	Commercial Production and Processing	275
8.4.1	Extrusion Processes	275
8.4.2	Processes for Manufacturing Moldable Polyolefin Beads	278
8.4.3	Cross-Linked Polyolefin Foam Sheet Processes	281
8.4.4	Cross-Linked Polyolefin Foam Bun Stock Processes	286
8.5	Applications	288
8.5.1	Fabrication	288
8.5.2	Major Applications	289
8.6	References	293
9	PVC Foams	301
9.1	Introduction	301
9.2	Characteristics of PVC	303
9.2.1	PVC Structures	304
9.2.2	Structure Changes During Processing	305
9.2.3	Influence of PVC Fusion on Physical Properties	305
9.3	Formulation Technology	305
9.3.1	Overview of Formulas for PVC Foam	305
9.3.2	Effects of Formulation Ingredients on the Foaming Process and Properties of Foamed Products	308
9.3.3	Use of Recycled PVC in Foam Formulations	317
9.3.4	Design of Experiment (DOE) for Foam Formulation Development	318
9.4	Processing Technology	320
9.4.1	Extrusion of PVC Foams	321
9.4.2	Injection Molding of PVC Foams	328
9.4.3	Foaming of PVC at Atmospheric Pressure	329
9.4.4	Microcellular PVC Foams	331
9.4.5	PVC/Wood Flour Composite Foams	334
9.5	Mechanical Property Analyses and Test Standards	335
9.5.1	Mechanical Properties	336
9.5.2	ASTM and ISO Standards	340
9.6	References	341
10	Epoxy Foams	347
10.1	Introduction	347
10.2	Epoxy Chemistry and Formulations	347
10.3	Blowing or Foaming Agents and Processes	349

10.3.1 Inert Gas Blowing Agents.....	350	12.2.3 Preparation.....	384
10.3.2 Inert Liquid Blowing Agents.....	350	12.3 Properties and Their Relationship to Structure.....	384
10.3.3 Reactive Blowing Agents.....	350	12.3.1 Structural Features.....	384
10.3.4 Expanding Synthetic Fillers.....	351	12.3.2 Physical Properties.....	384
10.3.5 Frothed Epoxies.....	352	12.4 Commercial Production and Processing.....	386
10.3.6 Epoxy Emulsions.....	352	12.4.1 Metering.....	386
10.3.7 Non-Aqueous Liquid Extractable Pore Formers and CIPS.....	352	12.4.2 Mixing.....	386
10.3.8 Solid Extractable Pore Formers.....	353	12.4.3 Dispensing.....	387
10.3.9 Stereolithography.....	353	12.4.4 Equipment Selection.....	388
10.4 Combinations of Epoxy and Isocyanate Based Thermosets.....	354	12.5 Applications.....	388
10.5 Three-Phase Synactics.....	355	12.5.1 Foam Applications.....	388
10.6 Fiber-Reinforced Foams.....	356	12.5.2 Forms of Foam.....	388
10.7 Removable Foams.....	356	12.5.3 Features of Silicone Products.....	388
10.8 Applications.....	357	12.5.4 Areas of Application.....	389
10.8.1 Automotive (also See Adhesive Applications Below).....	357	12.6 References.....	389
10.8.2 Electronics Encapsulation.....	359		
10.8.3 Adhesives.....	361	13 Fluoropolymer Foams.....	391
10.8.4 Building Retrofitting.....	361	13.1 History and Introduction.....	391
10.8.5 Dams, Tanks and Bridges.....	362	13.2 Chemistry and Physics of Foam Preparation.....	392
10.8.6 Expanding Cores.....	362	13.2.1 Nucleation and Bubble Growth.....	393
10.8.7 Sports Equipment.....	362	13.3 Properties and Their Relation to Cell Structure.....	397
10.8.8 Personal Care Products.....	363	13.3.1 Physical Properties.....	397
10.8.9 Thermoplastic Processing and Recycling.....	363	13.3.2 Thermal Properties.....	399
10.8.10 Lung Substitutes.....	363	13.3.3 Specific Heat.....	400
10.9 References.....	363	13.3.4 Electrical Properties.....	400
		13.4 Commercial Production and Processing.....	402
11 Latex Foam and Sponge.....	367	13.4.1 Foaming of FEP and PFA Resins.....	402
11.1 Introduction.....	367	13.4.2 Foaming of Fluoroelastomer Resins (such as Viton).....	403
11.2 Dunlop Process.....	369	13.4.3 Expansion of PTFE Resin.....	404
11.2.1 Compounding Ingredients.....	369	13.5 Applications.....	405
11.2.2 Processing Notes.....	370	13.6 References.....	406
11.2.3 Foaming.....	371		
11.3 Freeze Process.....	373	14 Wood Flour Composite Foams.....	409
11.3.1 Original Freeze Process.....	374	14.1 Introduction.....	409
11.3.2 Newer Freeze Process.....	374	14.1.1 Background on Polymeric Composites.....	409
11.4 Sponge.....	374	14.1.2 Natural Fibers and Their Properties.....	410
11.4.1 Open-Cell Sponge Rubber.....	374	14.1.3 Plastic/Wood Flour Composite Foams.....	413
11.4.2 Closed-Cell Sponge Rubber.....	375	14.2 Major Issues in Development of PWC Foams.....	415
11.5 References.....	378	14.2.1 Thermal Degradation of Natural Fibers.....	416
		14.2.2 Moisture Content and Volatile Emissions from Natural Fibers.....	418
12 Silicone Foams.....	379	14.2.3 Dispersion of Natural Fiber and Fiber-Matrix Bonding.....	420
12.1 Background and Development.....	379	14.2.4 Processing Difficulties Due to Increased Viscosity.....	421
12.1.1 Background.....	379	14.3 Phase Changes in Foaming of PWC.....	421
12.1.2 Development of Silicone Foams.....	379	14.3.1 Changes in Phase Morphology of the Extrudate During Microcellular Foaming and Fine-Cell PWC Foaming.....	421
12.1.3 Development of Flame-Retardant Foam Technology.....	381	14.3.2 Polymer/Gas Solution Formation.....	422
12.2 Chemistry and Preparation.....	381	14.3.3 Cell Nucleation.....	423
12.2.1 Foam Formation.....	381	14.3.4 Cell Growth Control.....	424
12.2.2 Optional Ingredients.....	381		

14.4 Experiments and Discussion.....	426
14.4.1 Effects of Volatile Emissions from Wood Flour During Extrusion Processing.....	427
14.4.2 Foaming Experiments with Varying Content of Extractives.....	431
14.4.3 Critical Processing Temperature in Extrusion Processing of PWC Foams.....	434
14.4.4 Foaming with Various CBAs.....	439
14.5 Conclusions.....	442
14.6 References.....	443
15 Phenolic Foams.....	447
15.1 Chemistry and Foam Formation.....	447
15.1.1 Phenolic Resins.....	447
15.1.2 Crosslinking of Phenolic Resins.....	449
15.1.3 Foam Formation.....	450
15.1.4 Reduction in Corrosivity of Phenolic Foam.....	452
15.2 Properties and Their Relation to Structure.....	452
15.3 Commercial Production and Processing.....	454
15.4 Applications.....	455
15.5 References.....	455
16 Flame Retardancy of Polymeric Foams.....	457
16.1 Introduction.....	457
16.2 The Combustion of Polymeric Foams.....	458
16.2.1 Flame Combustion of Polymeric Foams.....	458
16.2.2 Smoldering Combustion of Polymeric Foams.....	460
16.2.3 Filtration Combustion of Gases in Polymeric Foams.....	462
16.3 Test Methods and Fire Safety Classification Parameters of Foamed Materials for the Assessment of Fire Hazards.....	463
16.4 Recent Advances in Flame Retardancy of Polymeric Foams.....	468
16.4.1 The Development of Foams Based on Inherently Thermally Stable and Flame Retardant Polymers.....	468
16.4.2 Chemical and Physical Modification of Polymeric Foams.....	470
16.4.3 Additive Flame Retardants.....	471
16.5 References.....	475
17 Syntactic Polymer Foams.....	479
17.1 Introduction.....	479
17.2 Hollow Sphere Fillers.....	480
17.2.1 General Information.....	480
17.2.2 Glass Microspheres.....	480
17.2.3 Polymeric Microspheres.....	481
17.2.4 Miscellaneous Other Microspheres.....	482
17.2.5 Macrospheres.....	482
17.3 Syntactic Foam Processing.....	482
17.3.1 General Considerations.....	482
17.3.2 Rheology of Syntactic Mixtures.....	483
17.3.3 Casting and Molding Compositions.....	483

17.3.4 Regulating the Apparent Density.....	484
17.3.5 Microsphere Space Factors and Packing.....	485
17.4 Syntactic Foam Production.....	487
17.4.1 Epoxy Syntactic Foams.....	487
17.4.2 Oligoester Syntactic Foams.....	488
17.4.3 Phenolic Syntactic Foams.....	488
17.4.4 Organosilicone Syntactic Foams.....	489
17.4.5 Polyimide Syntactic Foams.....	489
17.4.6 Carbonized Syntactic Foams.....	489
17.4.7 Syntactic Prepregs.....	490
17.4.8 Miscellaneous Syntactic Foams.....	491
17.5 Physical Properties of Syntactic Foams.....	491
17.5.1 Strength Properties.....	491
17.5.2 Water Absorption and Resistance to Hydrostatic Pressure.....	494
17.5.3 Thermal Properties.....	496
17.6 Recent Developments and Main Applications.....	497
17.6.1 Sub-Sea and Shipbuilding Applications.....	497
17.6.2 Structural Applications.....	500
17.6.3 Aerospace Applications.....	502
17.6.4 Other Applications.....	503
17.7 References.....	503
18 Blowing Agents for Polymeric Foams.....	505
18.1 Introduction.....	505
18.2 Classification.....	505
18.3 Chemical Blowing Agents.....	507
18.3.1 Main Characteristics.....	507
18.3.2 Inorganic Blowing Agents.....	509
18.3.3 Organic Blowing Agents.....	511
18.3.4 Blowing Agents that Liberate Gases as a Result of Chemical Interaction between the Components.....	532
18.3.5 Practical Guide for Selection of CBAs.....	536
18.4 Physical Blowing Agents and Environmental Problems.....	539
18.4.1 Main Characteristics.....	539
18.4.2 Volatile Liquids.....	540
18.4.3 Solid Blowing Agents.....	546
18.5 Gases.....	546
18.6 Nucleazites.....	547
18.7 References.....	547
Appendix 1.....	549
Letters of the Roman Alphabet.....	549
Capital Greek Letters.....	550
Lower Case Greek Letters.....	551
Appendix 2.....	552
Conversion Factors between English and S.I. Units for Quantities Used in Describing the Physical Properties of Foams.....	552